

Surface-State Localization at Adatoms

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Low-temperature scanning tunneling spectroscopy of magnetic and non-magnetic metal atoms on Ag(111) and on Cu(111) surfaces reveals the existence of a common electronic resonance at an energy below the binding energies of the surface states. Using an extended Newns-Anderson model, we assign this resonance to an adsorbate-induced bound state, split off from the bottom of the surface-state band, and broadened by the interaction with bulk states. A lineshape analysis of the bound state indicates that native adatoms decrease the surface-state lifetime, while a cobalt adatom causes no significant change.

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The unique ability of scanning tunneling microscopy and spectroscopy (STS) to access locally the density of states of single adsorbed atoms and clusters has been recently used to investigate magnetic adatoms which – owing to the Kondo effect – exhibit a sharp spectroscopic structure close to the Fermi energy E_F [1, 2, 3, 4, 5, 6]. Surprisingly, only few studies of metal surfaces have been reported for non-magnetic adatoms and for a wider energy range around the Fermi level [4, 7, 8, 9, 10]. There is a good reason to explore the physics beyond a narrow range around E_F . For instance, it is known that a localized attractive perturbation of a two-dimensional electron gas should result in the appearance of a bound state, split off from the bottom of the continuum, and with a wave function localized around the perturbation [11]. Surface and image-potential states represent an opportunity to investigate this scenario with STS. In fact, it has been predicted that bound states should appear around single alkali atoms on metal surfaces as a consequence of their attractive perturbation on these two-dimensional electron gases [12].

In this Letter, we present a comparative low-temperature STS study of a set of adsorbates on the Ag(111) and the Cu(111) surfaces. We show that the density of states (DOS) of single silver and cobalt atoms adsorbed on Ag(111), as well as single copper and cobalt atoms adsorbed on Cu(111), exhibit a resonance below the binding energy E_0 of the surface states of these substrates. Within the framework of a Newns-Anderson model extended to a two-band interaction, we assign this resonance to a bound state split-off from the bottom edge of the surface-state band. A lineshape analysis suggests that the scattering of the surface state at the adsorbate affects its lifetime, depending on the adatom nature. This appears to be a general property of atoms interacting with a two-dimensional electron gas.

The measurements were performed in a homebuilt ultra-high vacuum scanning tunneling microscope at a working temperature of $T = 4.6$ K. The Ag(111) and the Cu(111) surfaces were cleaned by Ar^+ sputter/anneal

cycles. The single copper and silver adatoms were created by controlled tip-sample contact, whereas the single cobalt atoms were evaporated onto the cold substrates by heating a degassed cobalt wire wound around a pure W wire ($> 99.95\%$). The evaporation, through an opening of the liquid helium shield of the cryostat, yielded a coverage of 3×10^{-3} ML (ML=monolayer). No appreciable increase of other impurities was detected. The spectra of the differential conductance of the tunneling junction, dI/dV versus V , where V is the sample bias measured with respect to the tip, were acquired via lock-in detection (the root-mean-square (rms) modulation was 1 mV in amplitude and ≈ 10 kHz in frequency) while the current feedback was open. The etched W tip was treated *in situ* by soft indentations into the surface, until adatoms were imaged spherically and tip-structure artifacts were minimized near the dI/dV -voltages of interest. The thermalization of the substrate to 4.6 K ensured a negligible thermal diffusion of the adatoms within measurement times.

Figures 1 and 2 illustrate the main experimental findings. A dI/dV spectrum acquired over a bare terrace of Ag(111) is presented in Fig. 1a. The DOS has a sharp step-like onset at an energy E_0 which corresponds to the lower edge of the Ag(111) surface-state band, with a typical width governed by the surface-state lifetime \hbar/Γ . A similar onset is observed over a terrace of Cu(111) (Fig. 2a). Following Ref. 13, we extract $E_0 = -67(1)$ meV and $\Gamma = 7(1)$ meV from the Ag(111) onset, and $E_0 = -445(1)$ meV and $\Gamma = 24(1)$ meV from the Cu(111) onset, in agreement with recent lifetime measurements by angle-resolved photoemission [14]. The spectrum acquired over the center of individual atoms adsorbed on these surfaces differs substantially from the surface state spectrum as shown in Fig. 1b for a silver adatom (Ag) and a cobalt adatom (Co) on Ag(111), and in Fig. 2b for a copper adatom (Cu) and a cobalt adatom on Cu(111). The step-like feature at E_0 is lost, and new features appear in the DOS of the adsorbates: a resonance below E_0 (labeled **A**), and, in addition for the

FIG. 1: dI/dV spectrum over: (a) Center of a $20 \times 20 \text{ nm}^2$ defect- and impurity-free area of Ag(111), (b) Center of a silver atom and of a cobalt atom on Ag(111) (feedback loop opened at $R = 200 \text{ M}\Omega$, spectra are shifted vertically for clarity). Light-colored solid lines: fits described in the text.

FIG. 2: dI/dV spectrum over: (a) Center of a $20 \times 20 \text{ nm}^2$ defect- and impurity-free area of Cu(111), (b) Center of a copper atom and of a cobalt atom on Cu(111) (feedback loop opened at $R = 100 \text{ M}\Omega$, spectra are shifted vertically for clarity). Light-colored solid lines: fits described in the text. *Inset:* Kondo-Fano resonance of Co/Cu(111) near E_F .

cobalt atoms, a resonance near the Fermi energy (labeled **B**). When the tip is moved laterally off the center of the adsorbates, all features continuously decrease in amplitude and vanish at $\approx 10 \text{ \AA}$ away from the center. At a distance of $\gtrsim 50 \text{ \AA}$, the DOS of the surface-state is recovered. When decreasing the tunneling resistance over three orders of magnitude, corresponding to a height change between tip and adsorbate of approximately 3 \AA , feature **A** remains unchanged, except for a shift of the spectrum to lower energies, similar to the Stark shift observed for surface-state electrons [15]. The observation of feature **A** and its interpretation are the main topics of this Letter.

The structure near the Fermi energy (feature **B**) on cobalt is a Kondo resonance, which is detected as a Fano

FIG. 3: dI/dV images of a cobalt adatom near a monoatomic step of Ag(111) ($16 \times 16 \text{ nm}^2$, $I = 0.5 \text{ nA}$, $V = 100 \text{ mV}$). (a) Prior, (b) After manipulation (at 8 \AA from the step). Cobalt atoms are moved at $I = 50 \text{ nA}$ and $V = 2.8 \text{ V}$. (c) dI/dV spectra of a cobalt adatom at 24, 13 and 8 \AA from the bottom edge of a monoatomic step of Ag(111) (feedback loop open at $R = 200 \text{ M}\Omega$).

line in the dI/dV spectrum [1, 2, 4, 6, 16]. Since its first observation, several STS studies have reported similar resonances for a variety of Kondo systems [3, 4, 5, 6]. The Fano fit of various cobalt spectra yielded Kondo temperatures $T_K = 83(10) \text{ K}$ and $T_K = 63(6) \text{ K}$ for, respectively, Co/Ag(111) and Co/Cu(111), in agreement with previous studies on these systems.

The comparison between the Ag/Ag(111) and the Co/Ag(111) spectra, or between the Cu/Cu(111) and the Co/Cu(111) spectra, is a clear indication that feature **A** is related to a non-magnetic effect contrary to the Kondo effect of the cobalt atoms. Since this feature is observed in the same energy range for Co and Ag on Ag(111), and for Cu and Co on Cu(111), it is also unlikely that this resonance reflects an atomic orbital of the adsorbate, for example a cobalt d state. It must rather be related to the surface-state electrons of these surfaces, since the resonance occurs slightly below E_0 regardless of the adsorbate. To probe a possible surface-state involvement, additional spectroscopic information can be gathered by a close inspection of the adatom DOS near a monoatomic step edge of Ag(111) (Fig. 3). In this region, the back scattering of the surface-state electrons by the step leads to a standing wave pattern, which modifies the surface-state DOS [17, 18]. In the case of cobalt, the changes in the adatom spectra produced by this perturbation can be monitored by combining atom-manipulation and spectroscopy. Figures 3a and 3b illustrate two steps from a typical manipulation procedure for cobalt atoms, and Fig. 3c presents the spectra acquired over a cobalt adatom positioned at distances of 8, 13 and 24 \AA from the step edge. The overall structure of feature **A** changes in this region. A shoulder appears at -30 mV and the amplitude decreases as the cobalt atom is approached to the step. A similar behavior is also

Green's function techniques we obtain

$$n_a(E) = \frac{1}{\pi} \frac{\Delta(E)}{[E - \varepsilon_a - \Lambda(E)]^2 + \Delta(E)^2}. \quad (1)$$

The imaginary part of the self energy $\Lambda(E) + i\Delta(E)$ consists of contributions from the coupling of the adsorbate level to the bulk and the surface states, respectively: $\Delta(E) = \Delta_b(E) + \Delta_s(E)$. While the bulk contribution

$$\Delta_b(E) = \pi \sum_{\mathbf{q}} |V_{a\mathbf{q}}|^2 \delta(E - \varepsilon_{\mathbf{q}}) = \Delta_b$$

is taken to be constant over the energy range of interest, the surface state contribution

$$\Delta_s(E) = \pi \sum_{\mathbf{k}} |\tilde{V}_{a\mathbf{k}}|^2 \delta(E - \tilde{\varepsilon}_{\mathbf{k}}) = \Delta_s \Theta(E - E_0)$$

FIG. 4: Adatom DOS with a surface-state DOS (a) $n(E) = \Theta(E - E_0)$, (b) including lifetime effects. Dashed lines: without a coupling to the bulk states, solid lines: with a coupling to the bulk states. For clarity, part of the bound state is not shown in panel b.

observed for Ag/Ag(111), suggesting that this resonance has a strong surface state contribution. In contrast, the Kondo-Fano resonance does not reveal any appreciable change and T_K is constant in this region. While this may hint to a minor role for surface-state electrons in the Kondo effect of Co/Ag(111), a recent microscopic two-band theory of the surface-Kondo effect points to an intricate scenario [19].

From our experimental findings, we conclude that the resonance in the DOS of the adsorbates is surface-state-related. This appears to be a general property of noble-metal surface states, as a similar feature is also observed in STS of single atoms adsorbed on Au(111) [4]. Along the lines of Ref. 4, the most likely explanation for this resonance is that it is an adatom-induced-bound state, split off from the bottom of the surface-state band.

To model our data we start from a Newns Anderson Hamiltonian describing a single adsorbate level $|a\rangle$ of energy ε_a interacting with the bulk Bloch states $|\mathbf{q}\rangle$ [20], and add a second interaction to the surface states $|\mathbf{k}\rangle$ of the (111) substrate:

$$\mathcal{H} = \begin{pmatrix} \varepsilon_a & V_{a\mathbf{q}} & \tilde{V}_{a\mathbf{k}} \\ \tilde{V}_{a\mathbf{q}}^* & \varepsilon_{\mathbf{q}} & 0 \\ \tilde{V}_{a\mathbf{k}}^* & 0 & \tilde{\varepsilon}_{\mathbf{k}} \end{pmatrix},$$

where $\varepsilon_{\mathbf{q}}$ and $\tilde{\varepsilon}_{\mathbf{k}}$ denote submatrices containing the eigenenergies of the bulk and the surface states, respectively, while $V_{a\mathbf{q}}$ and $\tilde{V}_{a\mathbf{k}}$ are the coupling matrix elements between the adsorbate level $|a\rangle$ and the bulk and surface states of the substrate (here \mathbf{k} labels a two-dimensional Bloch wave vector, while \mathbf{q} is a three-dimensional vector). The tunneling spectrum with the tip at the position of the adsorbate atom is represented, with respect to all spectral features, by the projected DOS at the adsorbate atom $n_a(E)$. Applying standard

is assumed to be governed by the step-function like behavior of the surface state. The real part of the self energy follows from $\Delta(E)$ via a Hilbert transform. The stepped surface-state DOS results in a logarithmically divergent term at E_0 as remarked by Borisov *et al.* [21],

$$\Lambda(E) = \frac{\Delta_s}{\pi} \ln |E - E_0| + \text{const.},$$

where the constant term is absorbed in a renormalized eigenenergy ε'_a of the adsorbate level. The DOS at the adsorbate $n_a(E)$ is presented in Fig. 4a. Considering first only the coupling of the adsorbate to the surface state (dashed line in Fig. 4a), the adsorbate-substrate interaction produces at the adatom site in case of $\varepsilon_a > 0$ a bound state at an energy below, but exponentially close to the surface state continuum. The additional coupling to the bulk states broadens then the bound state into a resonance (solid line in Fig. 4a).

For a quantitative analysis of our results we need to model the surface state DOS as accurately as possible. This is done by including lifetime effects in the surface-state electrons leading to a smoother onset of the band edge at E_0 as seen experimentally (Figs. 1a and 2a). Following Ref. 22, we model the surface-state DOS as $n(E) = 1/2 + \arctan[(E - E_0)/(\Gamma/2)]/\pi$, Γ being the inverse lifetime of the surface state. The real part of the self energy then reads $\Lambda(E) = \Delta_s \ln[(E - E_0)^2 + (\Gamma/2)^2]/2\pi + \text{const.}$ Consequently, the bound state acquires an increased linewidth (Fig. 4b), and a smoother variation near E_0 occurs. We have used this surface-state DOS to reproduce the experimental data. Results are shown as solid lines in Figs. 1b and 2b, and the corresponding fitting parameters are collected in Tab. I.

Given the strong coupling Δ_b to the bulk conduction band found, the adsorbate level $|a\rangle$ is most likely the outermost orbital of the adatoms considered here, a 4s

TABLE I: Parameters of Eq. 1 employed to reproduce the experimental data. E_0 was fixed to the surface-state energy onset (Figs. 1a and 2a). Γ_0 is the inverse surface-state lifetime extracted from the surface-state DOS of the clean surfaces.

	ε'_a (eV)	Δ_b (eV)	Δ_s (eV)	Γ (meV)	Γ_0 (meV)
Ag/Ag	0.5(2)	0.8(2)	0.5(2)	12(1)	7(1)
Co/Ag	0.5(1)	0.7(1)	0.4(1)	7(1)	7(1)
Cu/Cu	-0.2(2)	0.9(3)	0.3(1)	35(5)	24(1)
Co/Cu	0.1(2)	0.9(2)	0.3(1)	24(2)	24(1)

level for Co and Cu, and a 5s level for Ag. The d orbitals generally lead to resonances ≈ 0.1 eV wide in the adatom DOS [8], whereas widths of $\approx 1 - 2$ eV have been predicted for s resonances [23]. Density functional calculations for Ag/Ag(111) confirm this assignment, as the d states of Ag to lie more than 3 eV below E_0 . [24] As for the coupling to the surface-state conduction band, Δ_s is weaker than Δ_b for all adatoms, but close to the findings by Heller *et al.* of $\Delta_s \sim \Delta_b$ for adatoms forming a quantum corral [25].

Focusing on Γ , we find that the inverse lifetime required to model the DOS is larger for atoms adsorbed on Cu(111) compared to Ag(111), reflecting the slope change near E_0 in the spectra of Figs. 1b and 2b. This difference is related to the observed inverse lifetimes of the clean surfaces (denoted Γ_0 in Tab. I), which is larger for Cu [13]. However, while Γ is nearly identical to Γ_0 for cobalt adatoms, a 50 % increase of Γ compared to Γ_0 is observed for the native adatoms. While an increased value of Γ is consistent with the result of a recent photoemission study of the scattering of image-potential states by Cu atoms on Cu(001) [26], the intriguing difference between Co and native adatoms deserves further investigation.

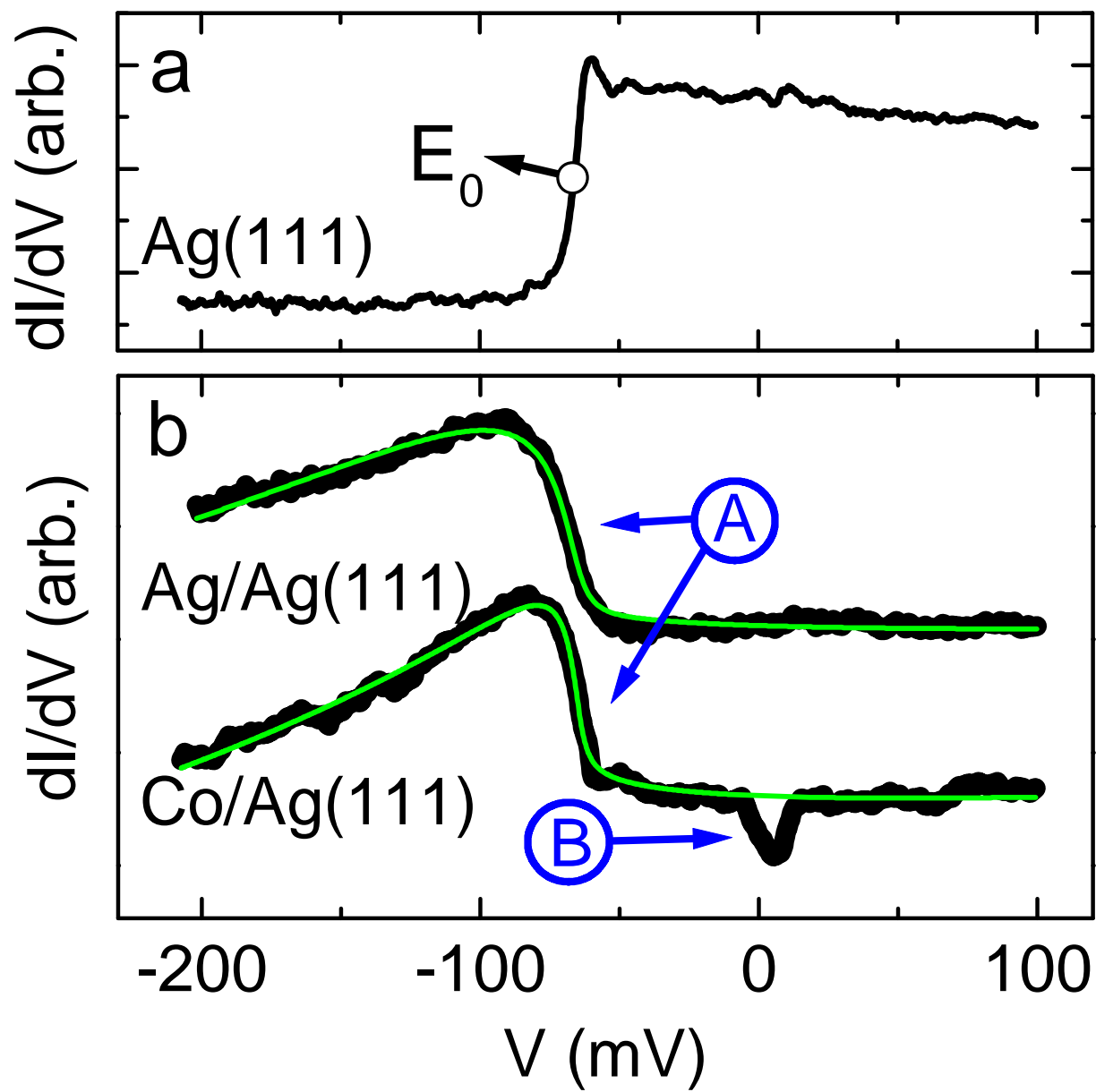
STS of Ag-clusters on Ag(111) (not shown) also reveals the existence of a feature at E_0 , suggesting that a bound state is produced regardless of the type of adsorbate – atom or molecule. In fact, the unique condition for a bound state to exist is that an energy level of the adsorbate must be coupled to the surface-state conduction band. However, its hybridization with the surface band structure and any change in the DOS of the surface-state electrons – for example near a step edge of the surface (Fig. 3) or in a nano-cavity – will modify the spectroscopic signature of the bound state.

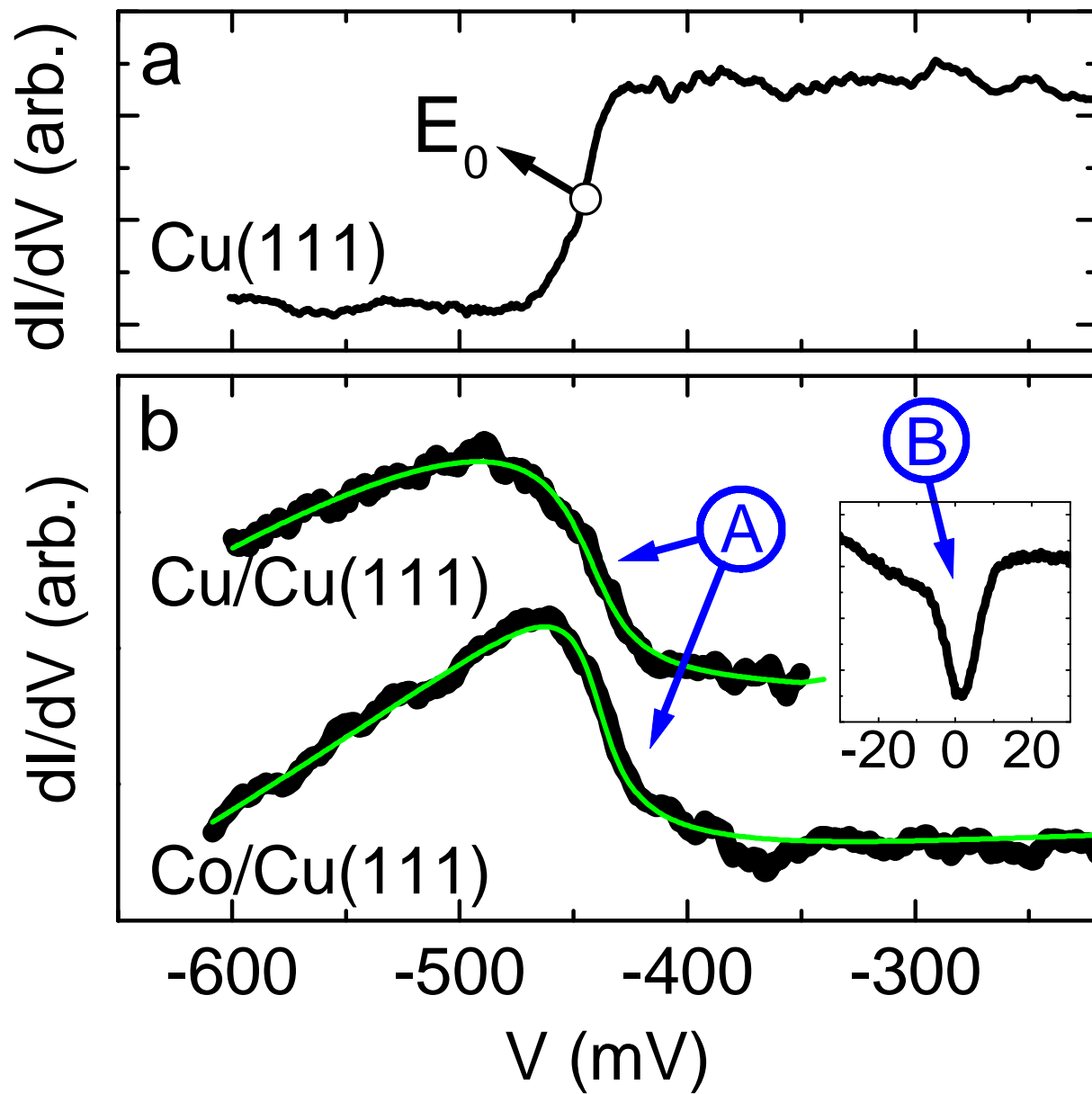
To summarize, single magnetic and non-magnetic atoms interacting with surface-state electrons produce a bound state in a energy range exponentially close to the surface-state low band edge. The bound state results from the coupling of the adatom's outermost orbital with the surface-state electrons, and is broadened by the interaction with bulk electrons. An analysis of the bound-state lineshape indicates that the surface-state lifetime is altered by the presence of the native adatoms whereas Co

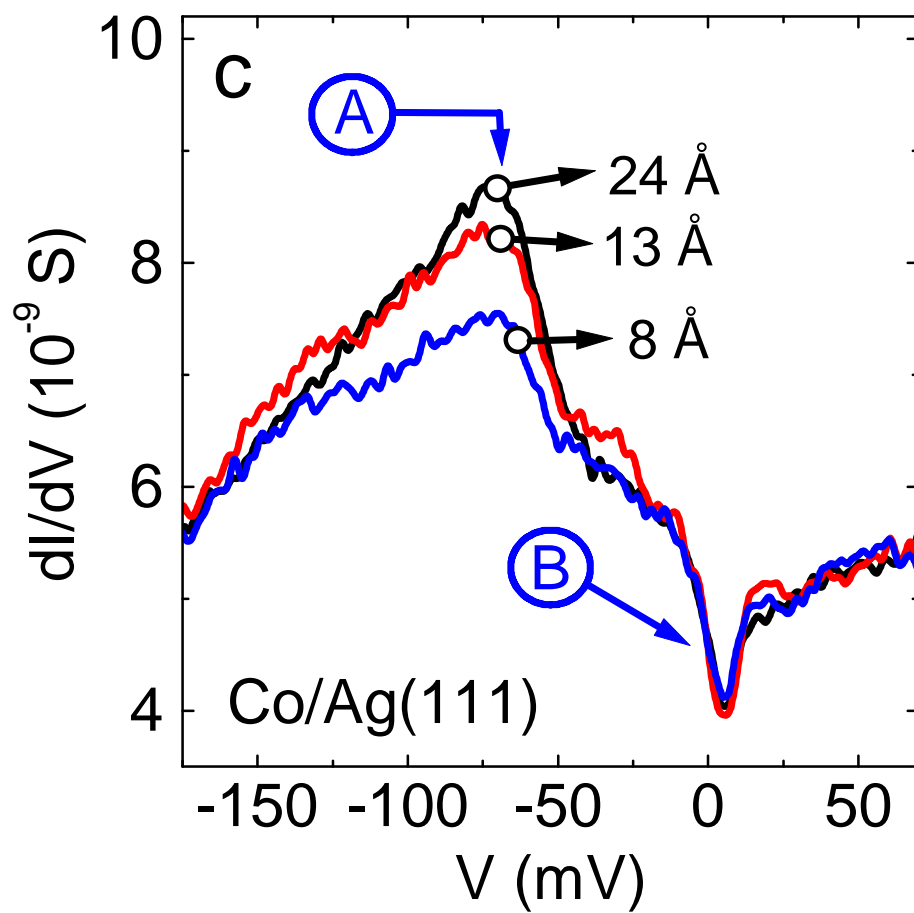
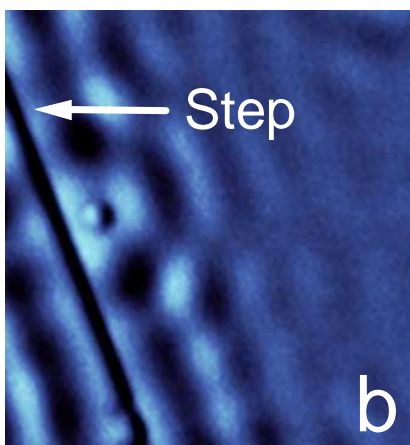
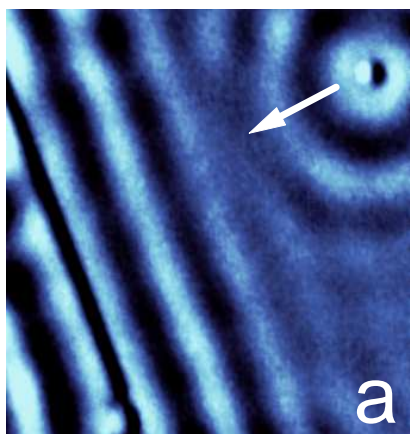
adatoms do not cause a prominent change.

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Adsorbate DOS $n_a(E)$

